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The effect of bonding on the fragmentation of small systems

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ABSTRACT

Recent dissociative recombination (DR) experiments have reported that the observed reaction products depend on the structure, bonding, and charge centre of the molecular ion. For examples, the dominant product channel observed in the DR of D_5^+ (2), $N_2O_2^+$ (1), and $D_5O_2^+$ (3) suggests that the former two ions have the form $D_3^+ \cdot D_2$, and $NO^+ \cdot NO$ (1), respectively, whilst the latter is known to have the form $D_2O \cdot D^+ \cdot D_2O$ (3). Here we compare and contrast these observations by investigating the DR of one of the simplest such systems, $Li^+ \cdot H_2$. This system, a weakly bound cluster with the charge centre located on the lithium atom, will provide us with an excellent opportunity for investigating the role played by the type of bonds and charge centre in the DR process.

1. Introduction

Dissociative recombination (DR) is a process in which a molecular ion recombines with a low-energy free electron and subsequently dissociates into neutral fragments. For low temperature plasmas containing molecular ions, DR is the most important neutralising process and is therefore of great importance to the chemistry occurring in such diverse regions as interstellar clouds, planetary atmospheres and in semi-conductor etching.

Recent DR studies have focussed on polyatomic ions, driven mostly by the fact that given the apparent simplicity of the DR process, developing a general theory to predict product branching ratios for even the simplest polyatomic ions, e.g. XH_2^+ , has proven to be difficult. The earliest models suggested that the reaction would predominantly proceed via the least amount of internal rearrangement, i.e. fracture of the weakest X-H bond, producing $\text{H} + \text{XH}$. However, the majority of storage ring studies on the DR of such ions show a propensity for three-body break-up, i.e. $\text{X} + \text{H} + \text{H}$ (see (4) for a comprehensive list). It is worth noting that a recent theoretical models developed in the group of Greene for H_3^+ shows great agreement with experimental data (5; 6; 7). High quality experimental data on basic systems is needed to both illuminate the fundamental processes underlying DR and to provide much needed and valuable input to theoretical models.

To understand the dynamics occurring in such simple systems, the effect of the structure, bonding, and charge centre of the molecular ion needs to be investigated. Small molecular cluster ions represent good toy models and several systems have recently been investigated, for examples N_2O_2^+ , D_5^+ , and D_5O_2^+ . These systems are small enough to allow complete detection of the product fragments and represent systems for which there are several different bond types, i.e. dative, covalent, hydrogen, and dipole, and either localised or delocalised charge centres, and the combination of these will influence how the neutral molecular system dissociates. Based on the experimental data obtained on the DR of these systems, the simplest model system which combines all of the features just discussed was chosen for investigation, i.e. LiH_2^+ .

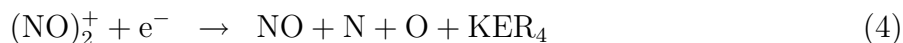
2. Dissociative Recombination in Storage Rings

All the experiments discussed in this paper were carried out at the heavy ion storage ring CRYRING, located at the Manne Siegbahn Laboratory, Stockholm University, Sweden. Such a facility has several experimentally desirable aspects for studies into DR. The ion-beam energies used are typically a few MeV. At such energies the electron capture cross section in collisions between the stored ion beam and residual gas molecules is small, which significantly reduces the contribution of background signals to the true data. For zero eV relative collisions between the electrons and the ions, it is much easier to create and control a stable and dense electron beam if the beam velocity is high, and this also requires MeV

ion beams. The good vacuum $< 10^{-11}$ Torr in the ring indicates that the number of residual gas molecules is extremely low, further decreasing the background contributions as well as enabling a long storage lifetime of the ion beam. This time, which can be tens of seconds, allows metastable and vibrationally excited components in the ion beam to decay to the ground state. A recent review on the use of merged-beams in atomic and molecular physics can be found in the literature(8).

3. Experimental Results and Discussion

In the collisions of D_5^+ , $D_5O_2^+$, and $N_2O_2^+$ with 0 eV electrons, the following reaction channels, with their associated kinetic energy release (KERn), are observed to be the most dominant:



It is noted that the available KER is a maximum for ground state fragments and the production of internally excited products reduces this. These results were obtained with the standard detection techniques used for obtaining chemical branching from DR and these techniques are discussed in Ref. (3).

The ionic structure, charge centre, and bonding of these ions is of relevance when analysing the dominant fragmentation channels. The weakly bound NO dimer ion has the form $NO^+ \cdot NO$ (1) while D_5^+ has the form $D_3^+ \cdot D_2$, i.e. it is a weakly hydrogen-bonded cluster, while $D_5O_2^+$ has a proton-bridge structure, and has an almost linear geometry given by $D_2O \cdot D^+ \cdot D_2O$ (3). In each case, the dominant product channels observed in the DR reaction are similar to those which would be expected if the “solvent” neutrals played little or no role in the reaction, i.e. the dominant channels in the DR of $D_3^+ \cdot D_2$ is similar to that from the DR of $D(H)_3^+$ (9), and the completely dominant production ($> 90\%$ (3)) of $2D_2O + D$ from the DR of $D_2O \cdot D^+ \cdot D_2O$ would also be expected. For $NO^+ \cdot NO$ the only other significantly populated channel is $NO + NO$.

The question that arises from these results is how much of the available reaction energy has been used in excitation of the molecular fragments. This is an important aspect in the case of both $NO^+ \cdot NO$ and $D_3^+ \cdot D_2$ as this would illuminate the role played in the DR reaction by the solvent molecule(s). A technique is needed which can measure the kinetic energy given to the reaction fragments, and such a technique has been developed and used with great success in studying the DR of both diatomic and triatomic molecular ions. Using a

position-sensitive detector (briefly, a stack of multi-channel plates (MCPs), a phosphor screen and a photo-multiplier tube (PMT) (10; 11)) monitoring the position of the fragments from the DR reaction allows the kinetic energy given to the fragments to be determined.

An example of the power of this technique is given in the following example, where the kinetic energy given to the D and D₂O fragments from the DR of D₅O₂⁺ has been determined. The preliminary results are shown in Fig.1, together with a simulation of the experimental data. The simulation, described in detail in Ref.(10), indicates that up to 3 eV is used in exciting the molecular D₂O products, i.e. the fragments share kinetic energy of 2.1 eV. It is obvious that the D₂O molecules solvating the D⁺ play a significant role in the reaction after the initial electron attachment. The data obtained from the DR of the NO⁺·NO dimer ion has also been reported, as well as a discussion on the reaction dynamics (1). The data for D₃⁺·D₂ are under analysis.

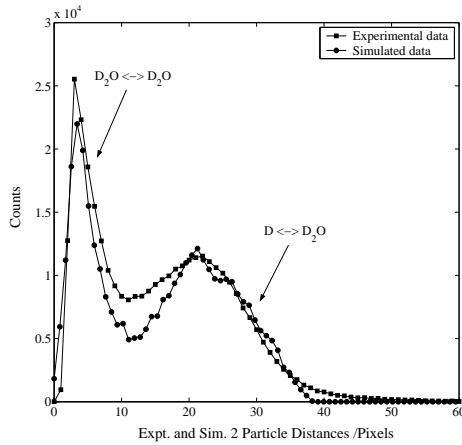


Fig. 1.— Distance distributions obtained from the DR of D₅O₂⁺.

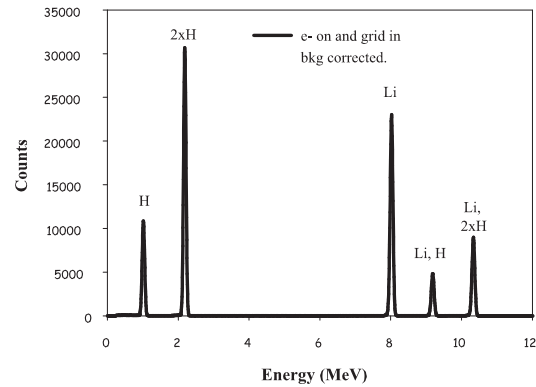


Fig. 2.— Multi-channel analyser data of the fragments produced from the DR of Li⁺·H₂.

Even from such preliminary analysis, the dynamics occurring in the dissociation step immediately following the attachment of the electron are very important for an understanding of the DR process. To help further understand the dynamics, a much simpler system was selected: the cluster ion Li⁺·H₂. This represents a nice model system. The charge centre is extremely localised on the lithium atom, the bonding between the Li⁺ and the H₂ molecule is controlled by the charge on the Li atom, i.e. is ion-induced, and the dative bond in the H₂ molecule is extremely strong in comparison. The neutral system, i.e. Li·H₂, is even more weakly bound than the ionic system, being Van der Waal's in nature.

An initial prediction for the DR reaction would be that only the channel producing Li + H₂ would be populated and any deviation from this would be illustrative of the post attachment interactions happening in a very weakly bound system. In 0 eV collisions the

following reaction channels, with their associated kinetic energy release (KER_n), are possible:



Preliminary data are shown in Fig. 2 where the peaks in the spectrum correspond to the various combinations of products possible in the reaction. Details on the data analysis techniques are discussed in Ref. (3). The results from this analysis shows that although the dominant channel populated in the DR reaction is that producing Li + H₂, i.e. channel (6), it is not the only channel. Just over a fifth of the reactions lead to the production of both LiH + H, and Li + 2H. These observations indicate that the post-attachment interaction is sufficiently strong, leading both to the fracture of the strongest bond in the system, the molecular hydrogen bond, and the formation of a much weaker-bonded molecular system, LiH.

4. Conclusions

In the light of recent experimental observations the development of a simple model to describe the DR process for even a small polyatomic ion does not seem to be a trivial matter. The preliminary results discussed here for the DR of some model systems show that the products depend on the structure, bonding, and charge centre of the molecular ion. The transition of the molecular system in moving from a single ionic state to an ensemble of highly-excited neutral states induces a dynamical interaction between the molecular and atomic constituents of the system. More work is needed to understand which types of interactions are the most dominant, and this could lead to the development of at least semi-empirical models.

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